STUDIES IN CONJUGATED SYSTEMS:

(I) THE ADDITION OF BROMINE TO 1-(P-BROMOPHENYL)-1,3-BUTADIENE

(II) THE ADDITION OF HYDROGEN BROMIDE TO 1-(P-BROMOPHENYL)-1,3-BUTADIENE

A THESIS

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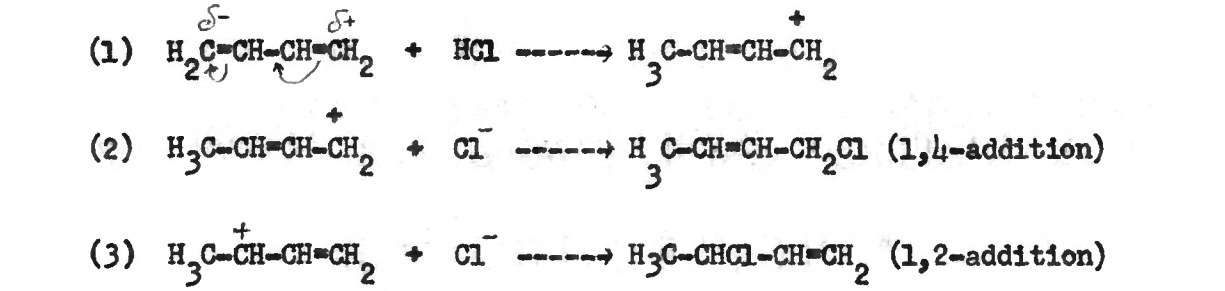
THEORETICAL

The problem of elucidating the mode of addition of halogens and halogen acids to conjugate systems has long been a problem of workers in this laboratory. These additions have been studied to a great extent in non-ionizing solvents and to a lesser extent in ionizing solvents.

The evidence of previous workers[1] has caused many to believe that 1,4-addition compounds do not form directly but result from the rearrangement of 1,2- or 3,4-addition reactions. It is clear that the reaction of hydrogen chloride with a conjugated diolefin should proceed by initial attack at a terminal carbon atom. The resulting intermediate is a mesomeric cation which may react at either of two positive centers to lead to 1,2- or 1,4-addition.



(1) $H_2\overset{\delta-}{C}=CH-CH=\overset{\delta+}{C}H_2 + HCl \longrightarrow H_3C-\overset{+}{C}H-CH=CH_2$

(2) $H_3C-\overset{+}{C}H-CH=CH_2 + Cl^- \longrightarrow H_3C-CH=CH-CH_2Cl$ (1,4-addition)

(3) $H_3C-\overset{+}{C}H-CH=CH_2 + Cl^- \longrightarrow H_3C-CHCl-CH=CH_2$ (1,2-addition)

It should be pointed out that there is a rather close resemblance between this modern interpretation of the additive reactions of conjugated dienes and Thiele's early interpretation[2] of the same phenomenon. If Thiele had had any concept of the electronic nature of the covalent linkage he probably would have proposed that a conjugated diene should

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[1] Thiele, Ann, 306, 87 (1899); 308, 333 (1899).

[2] Muskat and Northrup, J. Am. Chem. Soc., 52, 4043 (1930).

polarize in at least two ways. The following graphic examples will illustrate the possible electronic configuration of such a molecule:

$$\overset{+}{C} - C - C - \overset{-}{C} \quad \text{and} \quad \overset{+}{C} - \overset{-}{C} - C - C$$

1,4-addition 1,2-addition

Under these conditions it is possible for reactions to take place on adjacent or terminal carbon atoms of the chain.

Farmer, Thorpe and Northrup have shown that bromine adds to butadiene-1,3 in the 1,2-position[3] and undergoes rearrangement forming the more stable 1,4-addition compound. Results have also been obtained showing that bromine[4] and chlorine[5] add to 2,3-dimethylbutadiene-1,3 to form the stable 1,4-dihalide. It should be pointed out that although 1,4-addition of halogen is a characteristic behaviour of conjugated dienes, in general, a mixture of products is obtained. The driving force leading to 1,2- rather than 1,4-addition in the case of 1,4-diphenylbutadiene is probably due to the tendency of the remaining double bond of the product to be in conjugation with the aromatic ring. 1,4-Addition in this case would lead to a isolated double bond. It has also been pointed out that the bromination of 1-phenylbutadiene leads to addition of one mole of bromine at the 3,4-double bond.[6] It has been shown in this laboratory

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[3] Farmer, Thorpe and Northrup, J. Am. Chem. Soc., 730 (1928).

[4] Sweeting and Johnson, J. Am. Chem. Soc., 68, 1057 (1946).

[5] Jackson, "Chlorination of 2,3-dimethylbutadiene" (unpublished Master's thesis, Department of Chemistry, Atlanta University, 1935), p. 7.

[6] Muskat and Huggins, J. Am. Chem. Soc., 51, 2496 (1929).

that 1-phenyl-2,3-dimethylbutadiene-1,3 adds bromine in the same manner.[7] Hayes,[8] on the contrary, found that bromine added to 1-p-Nitrophenyl-2,3-dimethylbutadiene in the 1,4- position when methylene chloride was used as a solvent. She was unable to isolate any of the 3,4-adduct.

The introduction of an electron attracting group (the nitro group) in the ortho or para position of the phenyl ring decreases the electron density of the number one carbon and thus should enhance the addition of the negative bromide at that position.

Burton and Ingold[9] have emphasized the fact that in the addition of halogens to conjugated aryl dienes, phenyl-vinyl conjugation will always be preserved to the greatest possible extent. In addition, it has also been observed that phenyl-vinyl conjugation with its resonance effects stabilizes the adduct to the extent of about 7 kcal. per mole. It has been further observed that the greatest negative polarization occurs at the end of the conjugated system.

When phenyl-substituted butadiene is chlorinated or brominated, one may expect to obtain only equilibrium addition products. Since terminal initiation and phenyl-vinyl conjugation are the controlling factors in a conjugated system, one will be able to predict at least qualitatively the products of formation. For example, when phenylbutadiene is chlorinated

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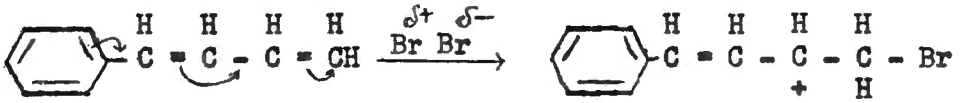
[7] McBay, "The Preparation and Bromination of 1-Phenyl-2,3-Dimethylbutadiene" (unpublished Master's thesis, Department of Chemistry, Atlanta University, 1936), p. 15.

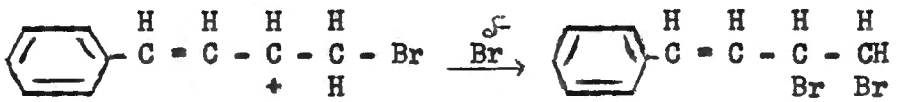
[8] Hayes, "The Bromination of 1-(p-Nitrophenyl)-2,3-Dimethylbutadiene-1,3" (unpublished Master's thesis, Department of Chemistry, Atlanta University, 1952).

[9] Burton and Ingold, J. Chem. Soc., 910 (1928).

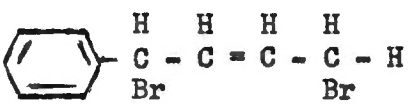
or brominated, the expected product will be the 3,4-dihalide.[10]

It has been experimentally shown [11] that when phenylbutadiene is chlorinated the 3,4-dihalide is obtained exclusively. On bromination of the same compound Strauss[12] was able to isolate only the 3,4-dihalide. The following equations will serve to illustrate this addition:





Only 3,4-addition in this manner permits utilization of the entire conjugated system in supplying electrons for the initial attack, retention of the resonance energy of the intact benzene ring and the formation of a product in which the remaining double bond is conjugated with the benzene ring. If the bromine had added in the 1,4- manner, phenyl-vinyl conjugation would be absent.



However, 1,4-addition can occur directly only if the phenylbutadiene molecule exhibits the polarizibility effect indicated below:

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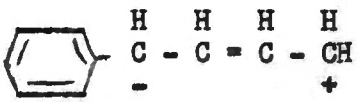
[10] De la Mare, Hughes and Ingold, J. Chem. Soc., 17 (1948).

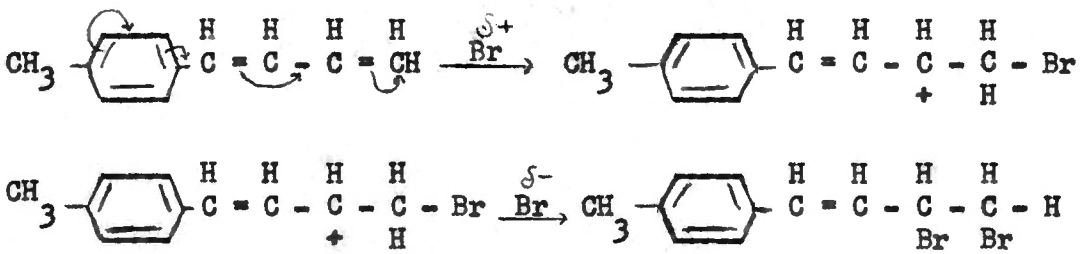
[11] Muskat and Northrup, J. Am. Chem. Soc., 52, 4043 (1930).

[12] Strauss, Ber., 42, 2867 (1909).



This structure exhibits wide charge separation, hence it is unstable. On the contrary, charge separation is lacking in the polarizibility effects which lead to 3,4-addition, and hence the retention of phenyl-vinyl conjugation.

It is apparent that one should be able to predict the mode of addition of halogen or halogen acids to mono substituted phenylbutadienes. For example, 1-(p-methylphenyl)butadiene should add bromine in the 3,4- manner. Since the methyl phenyl group is electron releasing and its polar effect can be transmitted down the entire conjugated system, carbon atom four should experience the greatest negative polarization. Therefore, the electrophilic bromine will attack at carbon atom four. The following equations illustrate this point:



Indeed, Anderson[13] observed that 1-(p-methylphenyl)butadiene-1,3 added bromine in the 3,4- manner to give a stable crystalline dibromide.

When the phenyl group in a mono substituted phenyl diene has an

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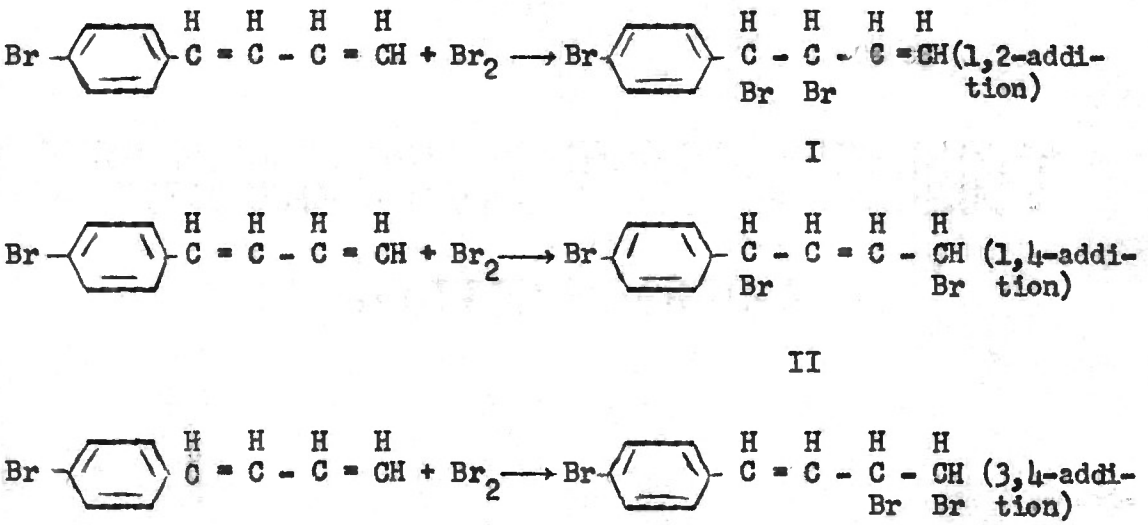
[13] Anderson, "Studies on 1-(4-Methylphenyl)butadiene-1,3" (unpublished Master's thesis, Department of Chemistry, Atlanta University, 1961).

electron attracting substituent in the para position, the stabilization due to phenyl-vinyl conjugation is decreased, consequently, 1,4-addition is expected. Hays[14] however, was unable to prepare the dichlore compound and only isolated a mono-chloride when he attempted to add a mole of chlorine to 1-(p-nitrophenyl)-2,3-dimenthylbutadiene-1,3.

In this study, 1-(p-bromophenyl)-1,3-butadiene was prepared and treated with bromine and hydrogen bromide in methylene chloride, a non-polar solvent. When the diene was brominated, three isomers were theoretically possible. The following equations illustrate the formation of these isomers:



Of the three isomers shown, only the isomer with structure (III) has the double bond conjugated with the benzene ring. It can be rationalized on the basis of the theory of phenyl-vinyl conjugation proposed by Ingold and modern electronic theory that the 3,4-addition product should result

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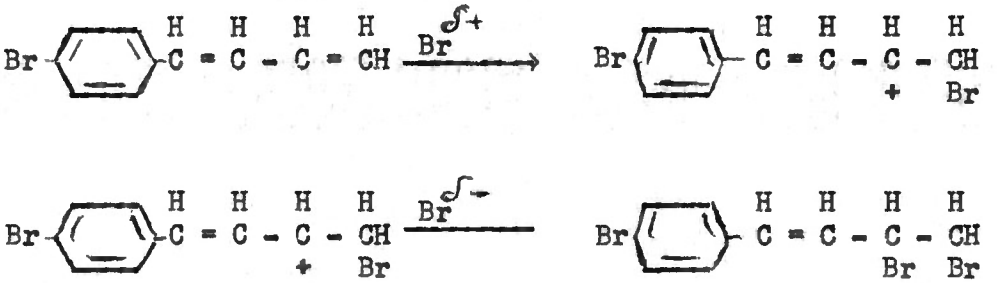
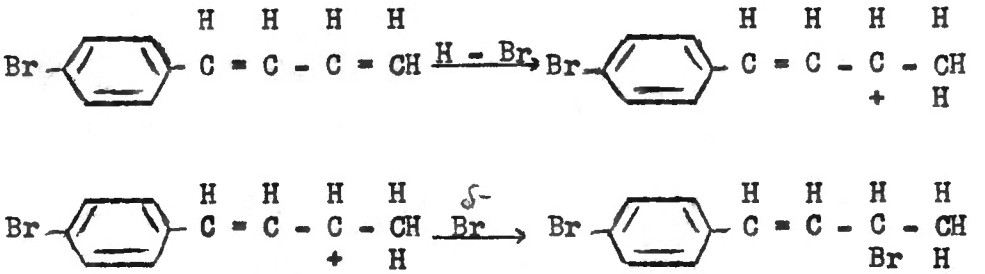
[14] Hays, "The Addition of Chloride to 1-(p-Nitrophenyl)-2,3-dimethylbutadiene-1,3" (unpublished Master's thesis, Department of Chemistry, Atlanta University, 1954).

when this diene is brominated. Indeed, it was proven by ozonolysis and ultraviolet absorption measurements that bromine added to 1-(p-bromophenyl)-1,3-butadiene in the 3,4- manner. Bromine and the phenyl group release electrons through resonance; therefore, this electron releasing effect will be transmitted down the conjugated system and carbon atom four will experience the greatest negative polarization. The electrophilic bromine will then attack the point of highest electron density, namely carbon atom four and the molecule exhibits the polarizibility effects shown:



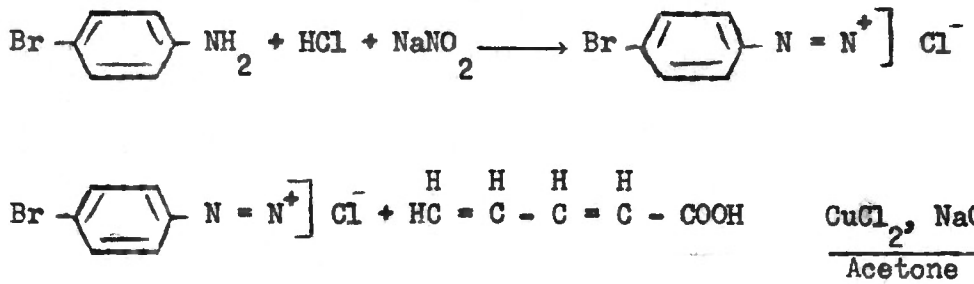
The stable crystalline 3,4-dibromide, melting range 72-73°, was isolated exclusively and it did not rearrange into the 1,4-dibromide. Although the bromine withdraws electrons inductively, apparently the effect is not powerful enough to induce a sufficiently positive charge on carbon atom one and thereby causing the bromine on carbon atom three to rearrange to position one to give the 1,4-dibromide. It should be noted that this study is limited to the thermodynamically controlled products and no attempt has been made to determine what the kinetically controlled products were. It would be interesting to carry out the addition of bromine in methanol and examine the methoxy bromides formed during the early stages of the reaction. If 3,4-addition predominates, it could be assumed that the 1,4-adduct had not intervened, because allylic rearrangement of the methoxy group is extremely unlikely.

In this investigation, hydrogen bromide was also added to 1-(p-bromophenyl)-1,3-butadiene in ether. The hydrogen bromide also added in the 3,4- manner.

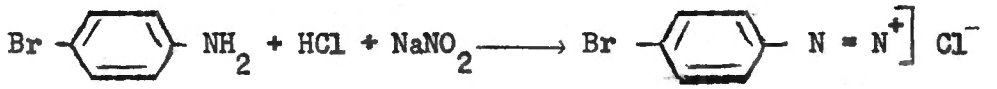


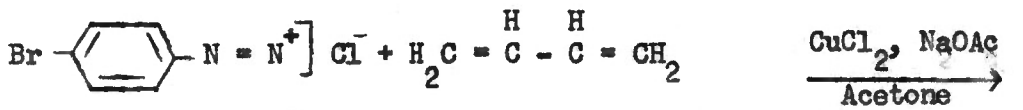
Phenylbutadiene and substituted phenylbutadiene with electron releasing groups in the para position add halogens and halogen acids in a 3,4- manner due to their ability to induce a high negative polarization on the carbon atom at the opposite end of the conjugated system. The 3,4-addition products formed do not rearrange into the 1,4-addition products.

The Meerwein reaction is commonly used to prepare mono substituted phenyl butadienes. 1-(p-Bromophenyl)-1,3-Butadiene could have been prepared by coupling p-bromobenzenediazonium chloride with vinylacrylic acid using cupric chloride as a catalyst, sodium acetate as a buffer and acetone as the solvent. The following equations illustrate this preparation:

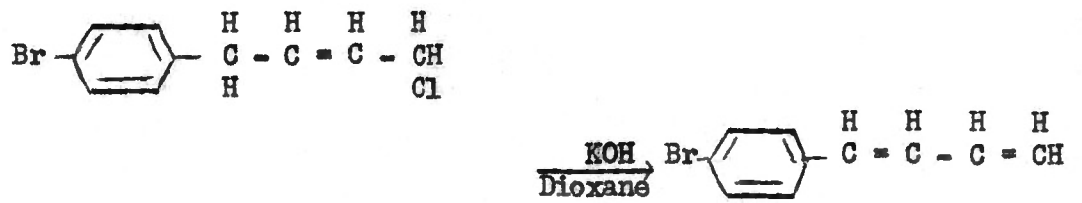


The 1-(p-bromophenyl)-1,3-butadiene, however, was prepared by coupling p-bromobenzene diazonium chloride with butadiene in the presence of cupric chloride as catalyst, sodium acetate buffer and acetone as a solvent. This procedure gives the corresponding chlorobutene. The following equations illustrate the preparation of the chlorobutene.

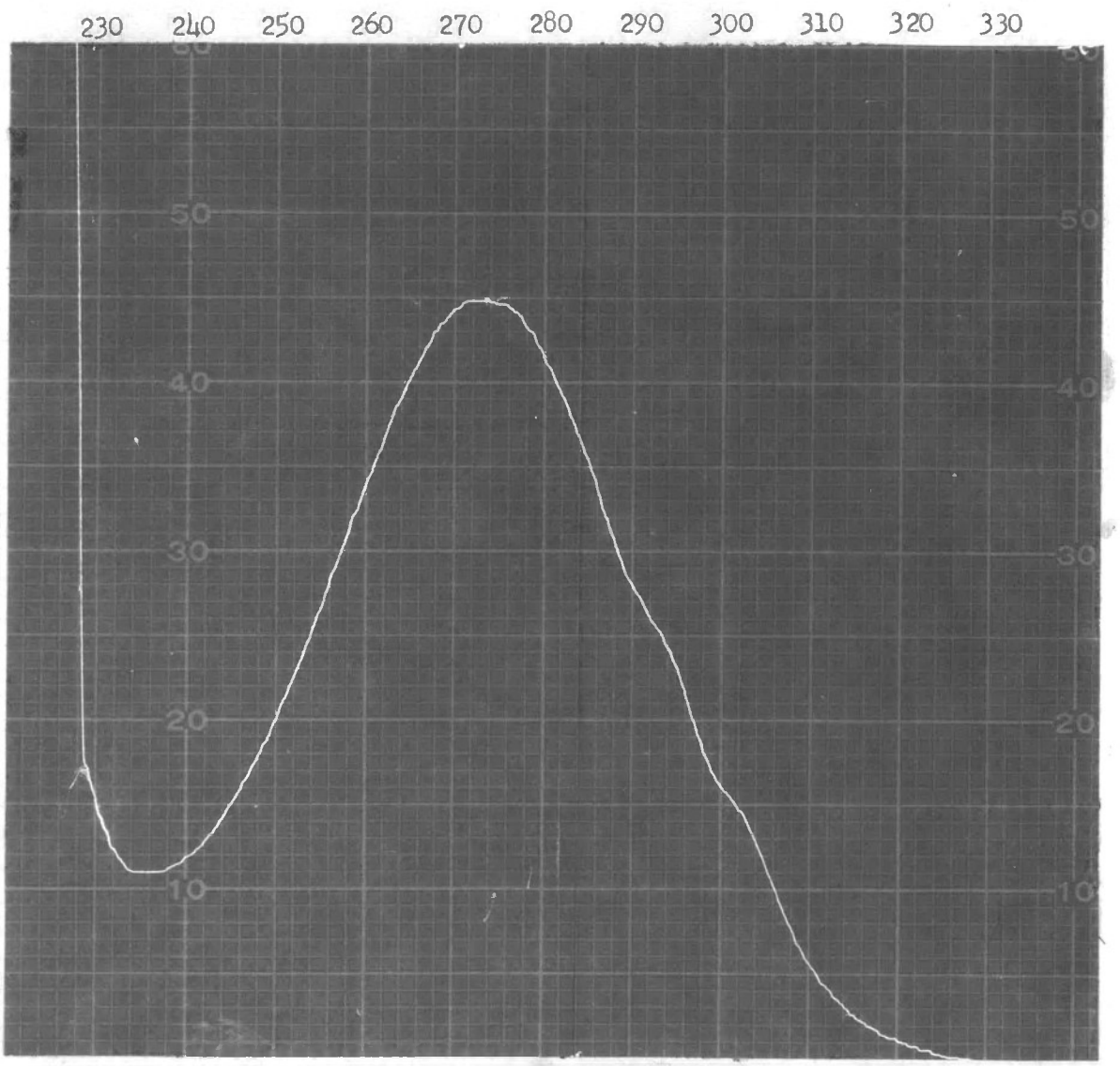




The dehydrohalogenation was effected by potassium hydroxide in dioxane. The following equation illustrate the dehydrohalogenation of the chlorobutene:



The ultraviolet plot of the dibromide as indicated on page eleven shows that there is a peak at about 274 millimicrons. For a phenyl-vinyl system without an alkyl group attached, the wave length would be in the range of 245-250 millimicrons, as in the case of styrene. The attachment of an alkyl group to the beta carbon shifts the wave length by about thirty millimicrons as is indicated for 1-(p-bromophenyl)-3,4-dibromo-1-butene. If an appreciable amount of 1,2- or 1,4-addition had occurred there should be a small peak in the range 245-250 millimicrons. Since there is no peak at this point there could hardly be any 1,2- or 1,4-adducts present.



Ultraviolet Spectrum of 1-(p-Bromophenyl)-3,4-dibromo-1-butene

EXPERIMENTAL

REAGENTS

p-Bromoaniline (M.P. 62-64°)
Matheson, Coleman and Bell

Acetone (B. P. 56°)
Commercial Solvent Corp.

Butadiene
The Ohio Chemical and Mfg. Co.

Hydrochloric Acid (Reagent Grade)
E. I. DuPont De Nemours and Company

Hydrogen Bromide (Anhydrous)
The Matheson Company, Inc.

Cupric Chloride
Baker Chemical Corporation

Sodium Acetate (Trihydrate)
C. P. Baker Company

Ligroin (90-120°)
Commercial Solvent Corp.

Ether (Reagent-Grade)
Merck and Company

Benzene (Thiophene Free)
Merck and Company

Methylene Chloride
Eastman Organic Chemicals

N-Heptane
Matheson, Coleman and Bell

Sodium Nitrite (Practical)
Eastman Organic Chemicals

Potassium Hydroxide
Baker Analyzed Reagent

Dioxane
Commercial Solvents Corp.

The Preparation of 1-(p-Bromophenyl)-4-Chloro-2-Butene.--1-(p-Bromophenyl)-4-Chloro-2-butene was prepared by a modification of the procedure described by Conyer and Ropp[14] in the Preparation of 1-(p-nitrophenyl)-4-chloro-2-butene. Forty-three grams (.25 Mole) of p-bromoaniline was dissolved in a hot solution of 60 ml. of concentrated hydrocholoric acid and 25 ml. of water. The solution was stirred rapidly and cooled in an ice-salt bath. After 25 g. of ice was added to the reaction mixture a solution of 17.5 g. of $NaNO_2$ (.25 Mole) in 30 ml. of water was dropped in during one hour while the temperature was kept between -4 and +4 degrees centigrade. Stirring was continued for an additional twenty minutes. At the end of this time urea was added until a negative test was given for nitrous acid with potassium iodide starch paper. The reaction mixture was filtered and the filtrate was kept below 4°C while it was added over a period of one hour to a well stirred mixture of 250 ml. of acetone, 20 g. of sodium acetate trihydrate dissolved in 25 ml. of water, 7.5 g. of cupric chloride dissolved in 30 ml. of water and 32 ml. of liquid butadiene. The reaction mixture was maintained between -3 and +2 degrees centigrade by means of an ice-salt bath during the addition and was then allowed to warm to room temperature. Stirring was continued for an additional 16 hours. Two hundred and fifty milliliters of ether were then added to extract the oily product and the ethereal solution was separated, washed four times with 250 ml. portions of water and dried over 10 g. of anhydrous sodium sulfate. Removal of the solvent at the water pump gave 36 grams of crude chlorobutene (58.8 per cent yield based on p-nitroaniline).

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[14] Conyer and Ropp, J. Am. Chem. Soc., 70, 2283 (1948).

The crude dark brown oil distilled at 117-121°C under 2 mm. pressure and yielded 22 g. of the pure chlorobutene ($N^{20}d$ 1.5709). When the chlorobutene was distilled rapidly the yield was slightly increased.

The Preparation of 1-(p-Bromophenyl)-1,3-butadiene.--In a dry round botton flask equipped with a reflux condenser and calcium chloride tube was placed 22 g. of 1-(bromophenyl)-4-chloro-2-butene, 15.5 g. (three fold molar) of potassium hydroxide and 50 ml. of dioxane. The contents were shaken until thoroughly mixed. This mixture was then refluxed for a period of 15 minutes. The hot mixture was poured into 250 ml. of water and the flask was washed with 50 ml. of water and these washings were added to the original mixture. The 1-(p-bromophenyl)-1,3-butadiene was extracted with ether. The ethereal layer was washed four times with 100 ml. portions of water and dried over magnesium sulfate. This ether solution yielded, 16.7 g. of the diene, boiling range 94-96°C under 2 mm. pressure, (87.4 per cent yield based on the chlorobutene).

The Reaction of Maleic Anhydride with 1-(p-Bromophenyl)-1,3-butadiene.--Maleic anhydride (.5 g.) and 1-(p-bromophenyl)-1,3-butadiene (1 g.) were refluxed for five minutes with 5 ml. of thiophene free benzene. On cooling, white crystals were deposited which crystallized from petrol (b.p. 80-100°) to yield 1.2 g. of adduct melting at 138.5-139°C. Braude[15] reported a melting point of 138.5°C.

The Reaction of Bromine with 1-(p-Bromophenyl)-1,3-butadiene.--The theoretical amount of bromine (2.2999 g.), dissolved in 100 ml. of methylene chloride, was added dropwise during 40 minutes to a solution of 3.004 g.

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[15] Braude, Stern and Jones, J. Chem. Soc., 1087 (1947).

of the diene in 250 ml. of methylene chloride at 0°C. At the end of the addition the solution was stirred for an additional two hours while cooled in an ice bath. This solution was then dried over night with anhydrous sodium sulfate. Removal of the solvent and recrystallization from heptane yielded 1.4 g. of the dibromide melting at 72°C.

Anal. Calcd. for $C_{10}H_9Br_3$: Br, 65.04. Found: Br, 64.96, 64.81.

The Ozonolysis of the Dibromo Compound.--In order to establish the structure of this dibromo compound, a 2 g. sample was dissolved in 150 ml. of methylene chloride and the solution was kept cold while ozonized oxygen was passed into the solution for a period of two hours. Removal of the solvent yielded the crude oily ozonide which was then heated on the steam bath with 50 ml. of water for two hours. This two phase mixture (solid-liquid) was extracted with ether and the ethereal layer was washed four times with 5 per cent sodium carbonate and then water to remove any acid that formed.

On acidification of the sodium carbonate solution a solid substance separated which was filtered and dried. This substance (7. g.) melted at 251°C which is the melting point of p-bromobenzoic acid. An authentic sample of p-bromobenzoic acid was mixed with the unknown sample and its presence did not alter the melting point. The ether was removed from the solution containing the neutral components, in vacuo, and a solid mass was left which melted with decomposition over the range 112-200°C. A small portion of this substance gave a negative test for aldehydes with 2,4-dinitrophenylhydrazine. Twenty-five milliliters of n-heptane was added to the solid mass and the mixture was heated and filtered while hot.

The filtrate yielded a crystalline substance (30 mg) which changed form at 112°C and as the temperature increased it decomposed slowly. The percentage bromine in this substance is very close to that in 1-(p-bromophenyl)-1,2,3,4-tetrabromobutane.

All attempts to isolate 1,2-dibromopropionic acid failed.

Anal. Calcd. for $C_{10}H_9Br_5$: Br, 75.84. Found: Br, 74.07.

The Reaction of Hydrogen Bromide with 1-(p-Bromophenyl)-1,3-butadiene in Ether.--A sample of 4.1022 g. of 1-(p-Bromophenyl)-1,3-butadiene was dissolved in 300 ml. of dry ether. A stream of anhydrous hydrogen bromide was bubbled through the mixture at 0°C with continued stirring for a period of three hours. Stirring was continued for an additional hour and the cold solution was transferred to a separatory funnel and washed with water and sodium carbonate solution until all of the excess hydrogen bromide was removed. The ethereal solution was allowed to stand over night on sodium sulfate. The next morning the ether was removed by suction at the water pump. Distillation of the remaining oil yielded 3 g. of monobromide, boiling range 130-134°C at 3 mm. pressure.

Anal. Calcd. for $C_{10}H_{10}Br_2$: Br, 55.17. Found: Br, 55.00, 55.04.

The Ozonolysis of the Hydohalogenated Product.--A slow stream of ozone was passed through a 2 g. sample of the monobromide dissolved in methylene chloride at 0°C, for four hours. Carbon dioxide was bubbled through the solution for five minutes to remove the excess ozone. The solvent was removed, in vacuo, and the remaining oil was refluxed with water for one hour. The soluble white crystalline solid was filtered off and proved to be p-bromobenzoic acid by the same procedure described earlier.

The water solution was extracted with ether and this ethereal solution was washed with 5 per cent sodium carbonate to remove any excess acid that might have been left in solution. On drying with sodium sulfate and removal of the solvent this solution yielded a lachrymator which we suspected to be 1-bromopropionaldehyde. Preparation of the 2,4-dinitrophenylhydrazone derivative of this substance, by a modification of the procedure described by Kirby,[16] yielded a substance that melted at 247-249°C. A positive Beilstein test on this derivative was obtained. A sample of 1-bromopropionaldehyde was prepared by the bromination of propionaldehyde[17] and the 2,4-dinitrophenylhydrazone derivative was made. The melting point of this derivative was 247-249°. A mixture of the two hydrazones did not show any depression in the melting point.

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16 Kirby, J. Am. Chem. Soc., 74, 4332 (1950).

17 Nef, Ann. 335, 264 (1904).

SUMMARY

In this study, 1-(p-bromophenyl)-1,3-butadiene was prepared by coupling butadiene with p-bromobenzenediazonium chloride and dehydrohalogenating the resulting chlorobutene to the diene.

The diene was brominated in methylene chloride, and the 3,4-addition product was obtained exclusively. Hydrogen bromide also added to the diene to yield the 3,4- isomer.

Ultraviolet absorption measurements and ozonolysis were used to determine the mode of addition of bromine and hydrogen bromide to 1-(p-bromophenyl)-1,3-butadiene.

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